

**Polydomain ferroelectricity in very thin films**  
[D.J. Kim *et al.*, Phys. Rev. Lett. **95**, 237602 (2005)]

T.W. Noh and his group (Kim *et al.*[1]) have recently published a seminal experimental study of very thin ferroelectric (FE) BaTiO<sub>3</sub> capacitors. They found an evidence that all their samples, including the thinnest one ( $d = 5\text{nm}$ ), are multi-domain (MD). Under a high enough external field, the MD state goes over into polarization saturated state, perhaps a single domain (SD) one, which relaxes back due to domain wall motion if the external field  $E_0$  is reduced below a certain value  $E_0 = E_{0r}$ . Kim *et al.* have approximately identified this field as a depolarizing field due to incomplete screening by electrodes and claimed that it coincides with the one estimated from electrostatics. We found that such an interpretation does not apply and there is actually a very instructive disagreement between the theory and experiment.

Kim *et al.* have presented the polarization  $P(E_0)$  in their Fig. 1a. The linear part of the curve has been attributed to a SD state. To find out what the authors call a “spontaneous polarization”, they used linear extrapolation of  $P_0 = P(E_0)$  to  $E_0 = 0$ . In fact, the spontaneous polarization ( $P_s$ ) should be defined as the polarization when the electric field *in the FE* is zero,  $E_f = 0$  ( $E_f < 0$  at  $E_0 = 0$  because of incomplete screening by the electrodes). The value of  $P_s$  has to be calculated from their data with the use of the formalism [2] and the LGD theory coefficients found in e.g. [3]. The dependence of  $P_s$  on  $d$  proves to be weak, Fig. 1a (inset).

The idea of Kim *et al.* is that the polarization relaxation sets in (because of domains) when  $E_f$  becomes opposite to the polarization. Let us find the corresponding external field  $E_0 = E_{0b}$ . Since  $E_f = E_0 - 2\lambda P/(\epsilon_0\epsilon_e d)$  [2], then  $E_{0b} = 2\lambda P_s/(\epsilon_0\epsilon_e d)$  with  $\lambda = 0.8\text{\AA}$  ( $\epsilon_e = 8.45$ ) the screening length (dielectric constant) of the electrodes[1]. This field is  $\sim 60\%$  larger than that determined by Kim *et al.* as the external field  $E_0 = E_{0r}$  for  $d = 5\text{nm}$  (raw data), while at  $d = 30\text{nm}$  the difference practically vanishes, Fig. 1a. This means that while in relatively thick films the domains begin to appear at small fields opposing polarization[4], in the thinnest film (5nm) the field is quite large, estimated as  $-(490 \pm 70)\text{kV/cm}$  [2], and yet there is no polarization relaxation for at least  $10^3\text{s}$  [1]. At much shorter time intervals,  $\sim 10^{-3}\text{s}$ , the field is apparently present too (see below). This is qualitatively similar to a dependence of the Merz’s activation field on an application (switching) time and a film thickness, although the thickness dependence of the field at short application times is not captured by Merz’s empirical formula[4].

The hysteresis loop  $P = P(E_f)$  has an unusual *negative slope*, Fig. 1 (raw data for 2kHz,  $d = 5\text{nm}$ , Ref. 2 in [1]). The negative slope is a hallmark of MD state and was predicted for an ideal FE film in a capacitor with

a voltage drop across a “dead” layer near FE/electrode interface[5]. There are no dead layers in the present system but the same effect is at work because of a volt-

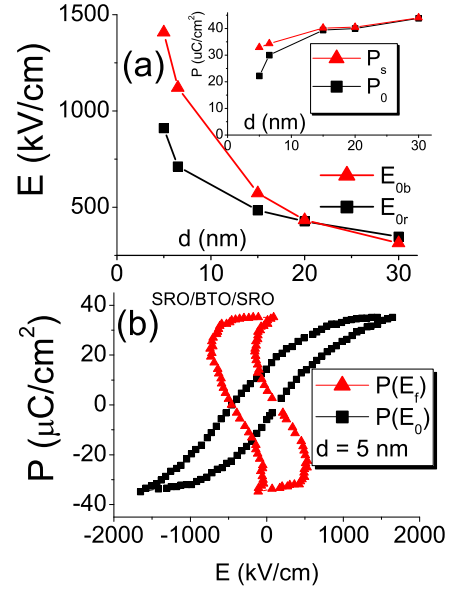


FIG. 1: (a) The external field  $E_{0b}$  (where  $E_f = 0$ ) and  $E_{0r}$  where the relaxation of polarization starts[1]. Inset: the spontaneous polarization  $P_s$  and the extrapolated  $P_0$ [1]. (b) The measured  $P(E_0)$  and the “actual”  $P(E_f)$  hysteresis loops.

age drop across a screening layer in the electrode with the thickness  $\lambda$ . Even numerically, the observed negative slope is surprisingly close to the theoretical value [2]. This means that in the thinnest films the behavior of the domain structure may be determined by the electrostatics rather than by pinning etc. If the value of the field promoting the domain formation is defined by the thickness only and not by properties of electrodes or an electrode-film interface, one can speculate about the properties of electrodes which can facilitate a smaller field in short-circuited sample and a longer retention of a SD state. We have found that for  $d = 5\text{nm}$  such an electrode should have  $\lambda/\epsilon_e < 0.03\text{\AA}$ . Since in [1] this value is about  $0.1\text{\AA}$ , it does not seem impossible to find such an electrode. Alternatively, thinner films may show longer retention. We thank T.W. Noh and his group for kindly sharing their data and many useful discussions. APL is partially supported by MAT2003-02600 and S-0505/MAT/000194.

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